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(54) Dispersing magnetic materials

(57) A dispersion of finely divided particles of a magnetic material in an organic liquid containing a dispersant comprising an amine carrying a poly(carbonylalkyleneoxy) chain (PCAO chain) in which the alkylene groups contain up to 8 carbon atoms, or an acid-salt thereof. The dispersion is useful for the preparation of magnetic recording media such as video, audio and computer recording tapes and discs. Certain of the dispersants are novel, especially a polyethyleneimine carrying at least two PCAO chains.

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SPECIFICATION

Dispersion

- 5 This specification describes an invention relating to a novel dispersion of finely divided magnetic particles, 5
to a novel dispersant, and to magnetic recording media made from the dispersion.

Magnetic recording media, such as video, computer and audio tapes and discs, generally comprise a non-ferromagnetic substrate, e.g. a polymeric material or a metal, carrying a superficial layer of magnetic particles contained in, and/or bound to, the substrate by a film-forming resin. Such recording media are 10
generally prepared by forming a dispersion of the magnetic particles in a solvent/resin system, applying the dispersion to the substrate and evaporating the solvent to leave a layer of resin and magnetic particles on the surface of the substrate. Before, or during, the drying operation the magnetic particles may be orientated by passing the substrate through a magnetic field. In order to improve the quality of the dispersion a dispersing aid, e.g. lecithin, a phosphate ester of an alkyl phenoxyethoxylate, a sulphosuccinate or a fatty acid salt, is 15
frequently added during the preparation of the dispersion. It has now been found that the magnetic properties of the recording medium, such as the "magnetic squareness", the "orientation ratio", the "remanent magnetic induction", the "switching field distribution" and/or the "coercivity" can be improved by the incorporation of a new dispersant. To take advantage of the improved dispersion quality, parameters of the dispersion system, such as concentration of dispersant and magnetic material and milling conditions, 20
may have to be adjusted depending on the nature of the magnetic material.

According to the present invention there is provided a dispersion of finely divided particles of a magnetic material in an organic liquid containing a dispersant comprising an amine carrying a poly(carbonylalkyleneoxy) chain in which the alkylene groups contain up to 8 carbon atoms, or an acid salt thereof.

The magnetic material may be any such material used for the preparation of magnetic recording media, 25
for example, the magnetic oxides of transition metals such as iron and chromium, especially gamma-Fe₂O₃, Fe₃O₄, cobalt-doped iron oxides, CrO₂, ferrites, especially barium ferrites, and metal particles, especially metallic iron, nickel, cobalt and alloys thereof. By the term finely divided is meant that the particles are below 5 microns and more preferably below 1 micron. Magnetic particles are generally anisotropic and the above dimensions refer to the length of the particles in their longest dimension.

30 The organic liquid is preferably a solvent for the resin which provides a protective film around the magnetic particles on the substrate and bind the particles to the substrate. Resins suitable for this purpose are polyurethanes, vinylacetate/vinylchloride copolymers and their derivatives, polyesters, epoxy resins, phenoxy resins, cellulose nitrates, polyvinylidenedichloride/acrylonitrile copolymers, butadiene/styrene copolymers, butadiene/acrylonitrile copolymers, polyisocyanates and alkyd resins.

35 Such resins are generally soluble in polar organic liquids such as ketones, esters, ethers and amides and these are preferred organics liquids for the present dispersions. Specific examples of such liquids are methylethylketone, cyclohexanone, methylisobutylketone, tetrahydrofuran, the acetates and alkyl ethers of ethylene glycol and the C₁₋₄-alkylethers. Other less polar organic liquids, such as toluene and xylene, may be employed either in admixture with the abovementioned more polar solvents or alone, provided the resin is 40
soluble therein.

The amine preferably conforms to the general formula:



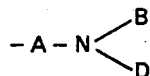
45 wherein 45
X is the poly(carbonylalkyleneoxy) chain;
Y is a bridging group; and
Z is an organic radical containing an amino group.

50 The alkylene groups in the poly(carbonylalkyleneoxy) chain, hereinafter referred to as "the PCAO chain", preferably contain from 3 to 6 carbon atoms, an especially preferred alkylene group being pentamethylene wherein the chain is a poly(6-hydroxycaproic) acid chain derivable from E-caprolactone. The PCAO chain may contain a mixture of alkylene groups of different length but is preferably a homopolymer. The PCAO chain may carry a chain-stopping terminal group at the free end, such as optionally substituted alkyl, e.g. 55
alkyl, alkoxyalkyl or haloalkyl, where the substituent prevents further growth of the PCAO chain. Where the dispersant is formed by the polymerisation of a carbonylalkyleneoxy monomer in the presence of an amine, the presence of a chain stopper is not necessary and the PCAO chain may be terminated by a hydroxy group. The PCAO chain preferably contains from 3 to 80 carbonylalkyleneoxy units.

The bridging group linking the PCAO chain to the amine is preferably an ester group, - CO - O -, but 60
more preferably an amide group, - CO - NR -, wherein R is H or C₁₋₂₀alkyl, especially C₁₋₄-alkyl, or a salt comprising two counter-ions attached to the amine and the PCAO chain, respectively, i. e. - CO - O⁻ NT₃⁺ -, in which T is H or an organic radical. The dispersant may contain more than one PCAO chain or may comprise a mixture of compounds, in which case it may contain a mixture of amide and salt links. The organic radical, T, may be aliphatic, alicyclic or aromatic or two of the groups, T, together with the nitrogen 65
atom may form a heteroalicyclic. Examples of organic radicals represented by T are methyl, thyl, lauryl,

stearyl, phenyl, benzyl, or T-groups may form a pentamethylene, an ethyleneoxyethylene or an ethyleneaminoethylene group.

The organic group, Z, is preferably of the general formula:



II

10 wherein

A is alkylene;

B is H, or optionally substituted alkyl; and

D is optionally substituted alkyl.

15 Where A, B or D represent or contain an alkylene group this is preferably a C₁₋₄-alkylene group where B or D is alkyl this may contain up to 20 carbon atoms which may be substituted by hydroxy, amino, halogen or alkoxy groups. Examples of the optionally substituted alkyl radicals represented by B and D are alkyl, such as ethyl, methyl, lauryl and octadecyl, aminoalkyl, such as aminoethyl and aminoethylaminoethyl, hydroxyalkyl, such as hydroxyethyl, hydroxyalkylaminoalkyl, such as hydroxyethylaminoethyl, aminoalkoxyalkyl, 20 such as aminoethoxyethyl, and poly(alkyleneimine). Where B and/or D represent poly(alkyleneimine) this is preferably poly(ethyleneimine) having a weight-average molecular weight up to 600,000 and may be branched or straight-chained.

The dispersant is derivable from an amine carrying an appropriate reactive group and a poly(carbonylalkyleneoxy) acid or a precursor thereof, such as a lactone. Where the bridging group is an ester, the dispersant may be derived from an amine carrying an hydroxy group and a PCAO acid, wherein reaction 25 between the hydroxy group on the amine and a terminal carbonyl group on the PCAO acid forms the ester linking group. Where the bridging group is an amide or a salt group, the dispersant may be derived from a polyamine, having at least one primary or secondary amino group, and a PCAO acid wherein reaction between a p- or s-amino group in the polyamine and a terminal carbonyl group on the PCAO acid forms the 30 amide or salt group. The dispersant is derivable from a wide range of amines from simple polyamines, such as dimethylaminopropylamine (DMAPA), diethylaminopropylamine (DEAPA), diethylenetriamine (DETA), triethylenetetramine (TETA), 3-dodecylamino- and 3-tetradecylamino-propylamine and 3-octadecylaminopropylamine (ODAPA), and aminoalcohols, such as diethylaminoethanol (DEAE), dimethylaminoethanol (DMAE) and triethanolamine (TEA), up to a large polymeric amine, such as poly(alkyleneimine), 35 e.g. poly(ethyleneimine) having a weight-average molecular weight up to 600,000. Where the amine contains two or more hydroxy and/or amino groups capable of forming ester, amide or salt groups, the dispersant may carry more than one PCAO chain, each being attached to the polyamine by an ester, amide or salt bridging group.

A preferred dispersant comprises a polyethyleneimine carrying at least two PCAO chains linked thereto by 40 amide and/or salt bridging groups. The polyethyleneimine may be straight-chained but is preferably branched-chained and, more preferably, with at least 10% of the nitrogen atoms being present in tertiary-amino groups.

The acid-salt form of the dispersant may be formed by reaction of the free amine form with an acid or by quaternisation of the amino group or groups to form a substituted ammonium ion or ions. Suitable reagents 45 for this purpose are mineral and strong organic acids or acidic salts, such as acetic acid, sulphuric acid, hydrochloric acid, alkylsulphonic acids, arylsulphonic acids and alkyl hydrogen sulphates and quaternising agents such as dimethyl sulphate (DMS), methyl and ethyl halides and diethyl sulphate (DES).

The dispersion preferably contains from 30% to 90% by weight of the magnetic material, based on the total weight of the dispersion and preferably from 0.25% to 10%, by weight, of the dispersant, based on the weight 50 of the magnetic material. Where the dispersion also contains a film-forming resin this is preferably present in an amount from 0% to 20%, by weight, based upon the total weight of the dispersion.

The dispersion may be prepared by mixing the magnetic material and the dispersant into the organic liquid, optionally with a suitable resin, and subjecting the mixture to a grinding operation to de-agglomerate the particles of the magnetic material and/or reduce the particles of the magnetic material to the appropriate 55 size. In order to maintain maximum anisotropy the grinding operation is continued for the minimum period of time required to reduce the particles or agglomerates thereof to the appropriate size. Suitable apparatus for the grinding operation is a ball or bead mill.

The present dispersion, when mixed with a film-forming resin, is particularly useful for application to an appropriate substrate, such as a polyester tape or disc or an aluminium disc, to form a magnetic recording 60 medium. The dispersion containing the resin may be applied to a tape or disc by a suitable coating technique and the organic liquid removed, by evaporation, to leave a film of the resin containing the magnetic particles evenly dispersed therein. The particles may be permanently oriented within the resin film by passing the tape or disc through a magnetic field immediately before or during evaporation of the organic liquid.

According to a further feature of the present invention there is provided a magnetic recording medium comprising a substrate carrying a superficial layer of a film-forming resin containing dispersed therein finely-divided particles of a magnetic material and a dispersant carrying a PCAO chain as hereinbefore defined.

- 5 Certain of the dispersants disclosed herein are novel compounds and according to a further feature of the present invention there is provided a dispersant comprising a poly(ethyleneimine) carrying at least two poly(carbonylalkyleneoxy) chains attached thereto by amide or a salt bridging groups in which the alkylene groups contain from 3 to 6 carbon atoms. It is preferred that the alkylene groups are all pentamethylene and that the PCAO chain contains from 3 to 80 carbonylalkyleneoxy units. 5
- 10 This dispersant may be prepared by reaction of a poly(ethyleneimine) with a PCAO acid or precursor thereof, such as a lactone or hydroxycarboxylic acid at a temperature from 25°C to 250°C for up to 24 hours. Under mild conditions (low temperature and/or short reaction time) salt bridging groups are formed and under more severe conditions (higher temperature and/or longer reaction time) amide or a mixture of amide and salt bridging groups are formed. 10
- 15 According to a further feature of the present invention there is provided an acid-salt of an amine carrying a poly(carbonylalkyleneoxy) chain attached thereto by an ester, amide or salt bridging group in which the alkylene groups contain from 3 to 6 carbon atoms. It is preferred that the alkylene groups are all pentamethylene and that the PCAO chain contains from 3 to 80 carbonylalkyleneoxy units. 15
- This dispersant may be prepared by reaction of an amine carrying an hydroxy group, or a polyamine 20 having at least one primary or secondary amino group, with a PCAO acid, or a precursor thereof such as a lactone or hydroxycarboxylic acid, at a temperature from 25°C to 250°C for up to 24 hours, and forming an acid-salt of the amine by reaction with an acid or a quaternising agent. 20
- The PCAO acid may be prepared by heating a hydroxycarboxylic acid or lactone with a carboxylic acid which is free from hydroxy groups, such as acetic acid, caproic acid, lauric acid and methoxyacetic acid. 25
- 25 Polymerisation is conveniently performed at a temperature from 100°C to 250°C, preferably from 130°C to 200°C, in the presence of an esterification catalyst, such as tetrabutyl titanate, zirconium naphthenate, zinc acetate or toluenesulphonic acid. 25
- To minimise degradation of the reactants and products the reactions are preferably performed under an inert atmosphere, such as nitrogen.
- 30 The invention is further illustrated by the following examples in which all parts and percentages are by weight unless otherwise indicated. 30

Dispersant 1

- A mixture of 111g of E-caprolactone, 8.1g of DMAPA and 0.1g of tetrabutyltitanate was stirred under nitrogen for 1½ hours at 175°C to 185°C. The product was a hard wax of equivalent 1604. 35

Dispersant 2

- A mixture of 230g of E-caprolactone, 8.1g of DMAPA and 0.1g of tetrabutyltitanate was stirred under nitrogen for 24 hours at 175°C to 185°C. The product was a hard wax of equivalent 3108. 40

Dispersant 3

- A mixture of 175g of E-caprolactone, 4.05g of DMAPA and 0.1g of tetrabutyltitanate was stirred under nitrogen for 12 hours at 210°C. The product was a hard wax of equivalent 4596. 45

- 45 *Dispersant 4*
A mixture of 150.6g of E-caprolactone, 8.1g of DMAPA and 0.1g of tetrabutyltitanate was stirred under nitrogen for 1½ hours at 160°C to 165°C. The product was a hard wax of equivalent 2050. 45

Dispersant 5

- 50 A mixture of 150g of E-caprolactone, 32.4g of DMAPA and 0.1g of tetrabutyltitanate was stirred under nitrogen for 7 hours at 170°C to 190°C. The product was a soft wax of equivalent 640. 50

Dispersant 6

- A mixture of 100g of Intermediate 3 and 10g of triethylene tetramine was stirred under nitrogen for ½ hour at 80°C. The product was a soft wax of equivalent 708. 55

Dispersant 7

- A mixture of 100g of Intermediate 3 and 20g of DUOMEEN C, a blend of alkyl diamines, predominantly 3-dodecylaminopropylamine and 3-tetradecylaminopropylamine, (DUOMEEN is a trade mark of AKZO 60 Chemie) was stirred under nitrogen for ½ hour at 80°C. The product was a soft wax of equivalent 1075. 60

Dispersant 8

A mixture of 66.8g of E-caprolactone, 8.85g of diethylethanolamine and 0.1g of tetrabutyltitanate was stirred under nitrogen for 1½ hours at 160°C to 165°C. The product was a hard wax of equivalent 1680.

Dispersant 9

A mixture of 102.5g of E-caprolactone, 10g of dimethylamino thanol and 0.1g of tetrabutyl titanate was stirred under nitrogen for 2 hours at 160°C to 165°C. The product was a hard wax of equivalent 1200.

5 *Intermediate 1* 5

A mixture of 112g of E-caprolactone, 9.2g of n-caproic acid and 0.1g of tetrabutyl titanate was stirred under nitrogen for 18 hours at 180°C to 190°C. The product was a hard wax with an acid value of 36mg KOH/g.

Intermediate 2

10 A mixture of 582g of E-caprolactone, 32.25g of methoxyacetic acid and 0.5g of tetrabutyl titanate was stirred under nitrogen for 20 hours at 170°C to 180°C. The product was a hard wax with an acid value of 35.2mg KOH/g. 10

Intermediate 3

15 A mixture of 500g of E-caprolactone, 73g of lauric acid and 0.5g of tetrabutyl titanate was stirred under nitrogen for 20 hours at 170°C to 180°C. The product was a hard wax with an acid value of 36.35mg KOH/g. 15

Intermediate 4

20 A mixture of 250g of E-caprolactone, 88g of lauric acid and 0.2g of tetrabutyl titanate was stirred under nitrogen for 8 hours at 160°C to 180°C. The product was a wax with an acid value of 75.7mg KOH/g. 20

Intermediate 5

25 A mixture of 485g of E-caprolactone, 34g of lauric acid and 0.1g of tetrabutyl titanate was stirred under nitrogen for 19 hours at 170°C to 190°C. The product was a hard wax with an acid value of 18.6mg KOH/g. 25

Intermediate 6

A mixture of 485g of E-caprolactone, 22.4g of lauric acid and 0.1g of tetrabutyl titanate was stirred under nitrogen for 19 hours at 170°C to 190°C. The product was a hard wax with an acid value of 12.4mg KOH/g.

30 *Intermediate 7* 30

A mixture of 500g of E-caprolactone, 17g of lauric acid and 0.1g of tetrabutyl titanate was stirred under nitrogen for 19 hours at 180°C to 200°C. The product was a hard wax.

Example 1

35 To 46.6g of Dispersant 4 stirring above its melting point (approximately 65°C) was added 2.7g of dimethylsulphate causing the temperature to rise by approximately 15°C. The mixture was then stirred for 1½ hours at 90°C to 100°C and cooled to ambient. The product was a hard wax, hereinafter called Dispersant 9. 35

40 *Example 2* 40

A mixture of 32.5g of Intermediate 1 and 1.25g of a dry polyethylenimine having a weight-average molecular weight in the region of 100,000, available from BASF under the name "POLYMIN Waterfree" (POLYMIN is a trade mark), was stirred under nitrogen for 8 hours at 120°C. The product was a wax of equivalent 3175, hereinafter called Dispersant 10.

45 *Example 3* 45

This was prepared in a similar manner to Example 2, but using 40g of Intermediate 1 and 3.33g of "POLYMIN Waterfree". The product was a wax of equivalent 1510, hereinafter called Dispersant 11.

50 *Example 4* 50

This was prepared in a similar manner to Example 2, but using 40g of Intermediate 1 and 13.3g of "POLYMIN Waterfree". The product was a sticky wax of equivalent 475, hereinafter called Dispersant 12.

Example 5

55 A mixture of 10.8g of the product of Example 2 and 10.8g of tetrahydrofuran was stirred and heated until a clear solution was obtained. The solution was cooled to 35°C and 0.405g of dimethyl sulphate was added. The mixture was then stirred for a further hour at 65-70°C. The tetrahydrofuran was then removed from the mixture by distillation, giving the product hereinafter called Dispersant 13. 55

60 *Example 6* 60

This was prepared in a similar manner to Example 5, but using 10.24g of the product of Example 3, 10.24g of tetrahydrofuran and 0.81g of dimethyl sulphate. The product is hereinafter called Dispersant 14.

Example 7

A mixture of 16.1g of the product of Example 4 and 16.1g of tetrahydrofuran was stirred and heated. A solution was obtained, but it was not completely clear. The solution was cooled to 40°C, and 4.05g of dimethyl sulphate was added slowly. There was a vigorous exotherm. The mixture was then stirred for a further hour at 65-70°C. The tetrahydrofuran was then removed from the mixture by distillation, giving the product hereinafter called Dispersant 15.

Example 8

This was prepared in a similar manner to Example 2, but using 95.7g of Intermediate 2 and 7.36g of "POLYMIN Waterfree". The product is hereinafter called Dispersant 16.

Example 9

This was prepared in a similar manner to Example 2, but using 97.3g of Intermediate 3 and 7.48g of "POLYMIN Waterfree". The product is hereinafter called Dispersant 17.

Examples 10 to 17

Table 1 lists a series of preparations carried out in a similar manner and at a similar temperature to Example 2, but using the starting materials, the weights thereof and the reaction times shown in the table.

TABLE 1

Example No.	Polyester component Intermediate No	Weight of Polyester component (g)	Weight of "Polymin Waterfree" used (g)	Reaction time (hours)	Product name Dispersant No
10	4	140	20	8	18
11	3	90	30	18	19
12	5	90	30	18	20
13	5	143	11	15	21
14	6	90	30	18	22
15	6	143	11	15	23
16	7	90	30	18	24
17	7	138	10.6	17	25

Example 18

65g of Dispersant 16 was stirred above its melting point (approximately 60°C) and 4.05g dimethyl sulphate added, causing the temperature to rise by approximately 15°C. The mixture was then stirred for 1½ hours at 85°C to 95°C. The product is hereinafter called Dispersant 26.

Example 19

This was prepared in a similar manner to Example 18, but using 68g of Dispersant 17 and 4.05g of dimethyl sulphate. The product is hereinafter called Dispersant 27.

Example 20

37.6g of Dispersant 8 was stirred above its melting point (approximately 45°C) and 2.7g dimethyl sulphate added, causing the temperature of rise by approximately 15°C. The mixture was then stirred for 2 hours at 85°C to 95°C. The product is hereinafter called Dispersant 28.

Example 21

A mixture of 100g of Intermediate 3 and 7.69g of polyethyleneimine, having a number average molecular weight of approximately 600, sold by the Dow Chemical Company under the name "MONTREK 6" (MONTREK is a trade mark), was stirred under nitrogen for 8 hours at 110°C to 130°C. The product was a hard wax, and is hereinafter called Dispersant 29.

Examples 22 to 24

Table 2 lists a series of preparations carried out in a similar manner and at a similar temperature to Example 1, but using the starting materials and the weights thereof shown in the table.

5	TABLE 2					5
10	Example No.	Polyester component Dispersant No	Weight of Polyester component (g)	Weight of dimethyl sulphate used (g)	Product name Dispersant No	10
	22	5	73	13.5	30	
	23	2	70.2	2.7	31	
	24	3	69	1.75	32	

15 *Example 25* 15

27.3g of Dispersant 9 was stirred above its melting point (approx 50°C) and 2.7g of dimethyl sulphate added, causing the temperature to rise by approximately 15°C. The mixture was then stirred for 2 hours at 85°C to 95°C. The product is hereinafter called Dispersant 33.

20 *Examples 26 to 60 and Comparative Examples (CE) 1 to 9* 20

Mixtures of magnetic material, dispersant, resin and solvent(s), as indicated in Table 3, were premixed using a high-speed stirrer and then subjected to a high energy ball-milling for the time shown in Table 3. Dispersions suitable for use in the manufacture of magnetic media were obtained in this way.

25 Examples 26 to 60 were made with Dispersants 1 to 33; Comparative Examples (CE) were made with Lecithin and GAFAC RE 610. 25

The magnetic materials used were as follows:

Type A A gamma-Fe₂O₃ with a surface area of 18.5m²/g, an oil absorption of 41ml/100g and a particle length of 0.4 microns. This is typical of magnetic iron oxides used in audio tapes.

30 *Type B* A cobalt-doped gamma-Fe₂O₃ with a surface area of 23m²/g, an oil absorption of 41g/100g and a particle length of 0.35 microns. This material which was supplied by Bayer UK Ltd. under the product name BAYFERROX AC 5120M (BAYFERROX is a trade mark) is typical of magnetic iron oxides used in high-bias audio tapes and in video cassette tapes. 30

35 *Type C* A stabilised magnetite with a surface area of 19m²/g, an oil absorption of 40g/100g, and a particle length of 0.45 microns. This material was supplied by Bayer UK Ltd., under the product name BAYFERROX AC 5110M. 35

Type D A chromium dioxide magnetic material of the type used in computer tapes and video cassette tapes.

Type E 99.99% pure Nickel supplied by the Aldrich Chemical Co Inc.

40 The resin was a hydroxylated vinyl chloride/vinyl acetate copolymer obtained from Union Carbide under the trade mark UCAR VAGH. 40

In the following tables the following abbreviations are used

45	THF	is tetrahydrofuran.	45
	MEK	is methyl ethylketone.	
	EOEA	is 2-ethoxyethyl acetate.	
	MIBK	is methyl iso-butyl ketone.	
	BA	is butyl acetate.	
	BOEA	is 2-butoxyethylacetate.	
	EA	is ethyl acetate.	
50	CH	is cyclohexanone	50
	Tol	is toluene	

GAFAC RE-610 is a phosphated alkylphenol-ethoxylate supplied by the GAF Corporation (GAFAC is a trade mark).

TABLE 3

<i>Example or CE 5 Number</i>	<i>Magnetic material & Amount (g)</i>	<i>Dispersant and Amount (g)</i>	<i>Solvent(s) and Amount (g)</i>	<i>Amount of resin (g)</i>	<i>High energy milling time (minutes)</i>	<i>5</i>
26	Type A 80.4	Disp.1 3.22	THF 36.98 MEK 36.98	2.41	30	
10 CE 1	Type A 80.4	Lecithin 3.22	THF 36.98 MEK 36.98	2.41	30	10
27	Type A 80.0	Disp.2 3.2	THF 37.2 MEK 37.2	2.41	60	
15 CE 2	Type A 80.0	Lecithin 3.2	THF 37.2 MEK 37.2	2.41	60	15
20 CE 3	Type A 80.00	GAFAC 3.2	THF 37.2 MEK 37.2	2.41	60	20
CE 4	Type B 20.0	Lecithin 0.8	THF 9.2 MEK 9.2	0.76	60	
25 28	Type B 20.0	Disp.17 0.8	THF 9.2 MEK 9.2	0.76	60	25
CE 5	Type B 20.0	GAFAC 0.8	THF 9.2 MEK 9.2	0.76	60	
30 29	Type B 20.0	Disp.18 0.8	THF 9.2 MEK 9.2	0.76	60	30
35 30	Type B 20.0	Disp. 21 0.8	THF 9.2 MEK 9.2	0.76	60	35
31	Type B 20.0	Disp.23 0.8	THF 9.2 MEK 9.2	0.76	60	
40 32	Type B 20.0	Disp.25 0.8	THF 9.2 MEK 9.2	0.76	60	40
33	Type B 20.0	Disp.19 0.8	THF 9.2 MEK 9.2	0.76	60	
45 34	Type B 20.0	Disp.20 0.8	THF 9.2 MEK 9.2	0.76	60	45
50 35	Type B 20.0	Disp.11 0.8	THF 9.2 MEK 9.2	0.76	60	50
36	Type B 20.0	Disp.13 0.8	THF 9.2 MEK 9.2	0.76	60	
55 37	Type B 20.00	Disp.16 0.8	THF 9.2 MEK 9.2	0.76	60	55
38	Type B 20.0	Disp.29 0.8	THF 9.2 MEK 9.2	0.76	60	
60 39	Type B 20.0	Disp. 6 0.8	THF 9.2 MEK 9.2	0.76	60	60

TABLE 3 (c ntinued)

<i>Example or CE 5 Number</i>	<i>Magnetic material & Amount (g)</i>	<i>Dispersant and Amount (g)</i>	<i>Solvent(s) and Amount (g)</i>	<i>Amount of resin (g)</i>	<i>High energy milling time (minutes)</i>	<i>5</i>
40	Type B 20.0	Disp. 7 0.8	THF 9.2 MEK 9.2	0.76	60	
10 41	Type B 16.0	Disp.17 0.64	THF 11.3 MEK 11.3	0.76	60	10
15 42	Type B 24.0	Disp.17 0.96	THF 7.14 MEK 7.14	0.76	60	15
43	Type B 20.0	Disp.17 0.4	THF 9.4 MEK 9.4	0.76	60	
20 44	Type B 20.0	Disp.17 0.8	THF 13.83 Tol 4.61	0.76	60	20
45	Type B 20.0	Disp.17 0.8	THF 6.15 MIBK 6.15 Tol 6.15	0.76	60	
25 46	Type B 20.0	Disp.17 0.8	CH 12.91 THF 5.53	0.76	60	25
30 47	Type B 20.0	Disp.17 0.8	EOEA 12.91 THF 5.53	0.76	60	30
48	Type B 20.0	Disp. 17 0.8	BA 12.91 THF 5.53	0.76	60	
35 49	Type B 20.0	Disp. 17 0.8	BOEA 12.91 THF 5.53	0.76	60	35
50	Type B 20.0	Disp.17 0.8	EA 9.2 THF 9.2	0.76	60	
40 51	Type A 20.0	Disp.17 0.8	THF 9.2 MEK 9.2	0.76	60	40
45 CE 6	Type A 20.0	Lecithin 0.8	THF 9.2 MEK 9.2	0.76	60	45
52	Type D 20.0	Disp.17 0.8	THF 9.2 MEK 9.2	0.76	60	
50 CE 7	Type D 20.0	Lecithin 0.8	THF 9.2 MEK 9.2	0.76	60	50
53	Type C 20.0	Disp.17 0.8	THF 9.2 MEK 9.2	0.76	60	
55 CE 8	Type C 20.0	Lecithin 0.8	THF 9.2 MEK 9.2	0.76	60	55
60 54	Type A 80.4	Disp.1 3.22	THF 36.98 MEK 36.98	2.41	60	60
CE 9	Type A 80.4	Lecithin 3.22	THF 36.98 MEK 36.98	2.41	60	

TABLE 3 (continued)

<i>Example or CE 5 Number</i>	<i>Magnetic material & Amount (g)</i>	<i>Dispersant and Amount (g)</i>	<i>Solvent(s) and Amount (g)</i>	<i>Amount of resin (g)</i>	<i>High energy milling time (minutes)</i>	<i>5</i>
55	Type A 80.4	Disp.1 6.41	THF 35.38 MEK 35.38	2.41	45	
10 56	Type A 96.0	Disp.1 3.92	THF 28.84 MEK 28.84	2.41	45	10
15 57	Type A 64.0	Disp.1 2.56	THF 45.52 MEK 45.52	2.41	45	15
58	Type A 80.4	Disp.1 3.22	THF 38.19 MEK 38.19	-	45	
20 59	Type A 80.0	Disp.2 3.20	THF 37.20 MEK 37.20	2.41	45	20
60	Type A 80.0	Disp.3 3.20	THF 37.20 MEK 37.20	2.41	45	
25	<i>Example 61</i>					25
	80g of magnetic material type E, 3.2g of Dispersant 17, 9.2g of THF, 9.2g of MEK and 0.76g of UCAR VAGH resin were loaded into a conventional ball mill charged with 600g of 7mm steel balls. After 7 days of milling, a dispersion suitable for use in magnetic media manufacture was obtained.					
30	Similar formulations in which Dispersant 17 was replaced by an equal weight of lecithin and an equal weight of GAFAC RE-610 solidified in the mill and failed to produce dispersions.					30
	<i>Examples 26A to 53A and Comparative Examples 1A to 8A</i>					
35	Dispersions prepared in Examples 26 to 53 and Comparative Examples 1 to 8 were let down with a 20% w/w solution of a polyurethane (PU) resin in tetrahydrofuran. Typically the let down was carried out in three stages with approximately equal quantities of polyurethane solution each time. The mixture was subjected to a 5 minute high-energy ball milling after each stage of the let down. The resultant lacquers were then further let down with solvent and the mixture subjected to a further 5 minutes high-energy ball milling. Table 4 identifies the dispersions, the weight of PU resin solution used in the let down and the weight of solvent used in the let down; unless otherwise indicate the let down solvent was a 1:1 mixture of tetrahydrofuran and methyl ethyl ketone. The PU resin used was obtained from B.F. Goodrich Inc. under the name ESTANE 5701-F1 (ESTANE is a trade mark).					35
40						40

TABLE 4

	<i>Example or CE Number</i>	<i>Dispersion used</i>	<i>Amount of 20% PU resin solution (g)</i>	<i>Amount of solvent used (g)</i>	
5	26A	Ex.26	68.2	119.6	5
	CE 1A	CE 1	68.2	119.6	
10	27A	Ex.27	76	119.6	10
	CE 2A	CE 2	76	119.6	
15	CE 3A	CE 3	76	119.6	15
	CE 4A	CE 4	22	14.92	
	28A	EX.28	22	14.92	
20	CE 5A	CE 5	22	14.92	20
	29A	Ex.29	22	14.92	
25	30A	Ex.30	22	14.92	25
	31A	Ex.31	22	14.92	
	32A	Ex.32	22	14.92	
30	33A	Ex.33	22	14.92	30
	4A	Ex.34	22	14.92	
35	5A	Ex.35	22	14.92	35
	36A	Ex.36	22	14.92	
	37A	Ex.37	22	14.92	
40	38A	Ex.38	22	14.92	40
	39A	Ex.39	22	14.92	
45	40A	Ex.40	22	14.92	45
	41A	Ex.41	17.6	3.94	
	42A	Ex.42	26.4	25.90	
50	43A	Ex.43	22	14.92	50
	44A	Ex.44	22	THF 14.92	
55	45A	Ex.45	22	THF 14.92	55
	46A	Ex.46	22	THF 14.92	
	47A	Ex.47	22	THF 14.92	
60	48A	Ex.48	22	THF 14.92	60
	49A	Ex.49	22	THF 14.92	
65	50A	Ex.50	22	THF 14.92	65

TABLE 4 (continued)

	Example or CE Number	Dispersion used	Amount of 20% PU resin solution (g)	Amount of solvent used (g)	
5	51A	Ex.51	22	14.92	5
	CE 6A	CE 6	22	14.92	
10	52A	Ex.52	22	14.92	10
	CE 7A	CE 7	22	14.92	
15	53A	Ex.53	22	14.92	15
	CE 8A	CE 8	22	14.92	
<i>Example 61A</i>					
20	Dispersion 61 was let-down with 40g of 20% PU resin solution and milled for 1 hour, let-down with a further 48g of 20% PU resin solution and milled for ½ hour, and then let-down with 50g of a 1:1 mixture of THF and MEK and milled for ½ hour.				20
<i>Magnetostatic evaluations</i>					
25	The let down lacquers were discharged from the ball-mill and used to coat a roll of 12 micron thick biaxially-oriented polyester film. In the case of Examples 26A and 27A and Comparative Examples 1A and 3A the coating was carried out using a gravure coater. Immediately after coating and before any appreciable drying, the film was passed between like poles of two powerful magnets. The film was then dried by solvent evaporation prior to winding.				25
30	In the case of Examples 28A to 53A and 61A and Comparative Examples 4A to 8A the coating was carried out using a mechanised wire-wound K-bar (Meyer Bar) draw-down system. The K-bar was calibrated to leave a wet film of thickness 50 microns. The machine was modified so that a powerful permanent magnet mounted about 1.5 cm above the polyester film followed the motion of the K-bar. In this way a strong magnetic field passed across the wet-film before any appreciable solvent evaporation had taken place. The film was then allowed to dry by solvent evaporation.				30
35	Samples of coated films were then evaluated by conventional techniques on a vibrating-sample magnetometer. The normal operating procedure with this equipment involved carry out measurements consecutively on a series of samples. In order to provide an internal control, and allow comparison between data relating to different series, a control was included in each series. This control was a Comparative Example containing the magnetic material under evaluation and Lecithin as the dispersant. Table 5 reports the magnetic parameters of coated films determined in ten series of consecutive measurements. The first sample in each series is the control.				35
40	The magnetic parameters determined were coercivity (in Oersteds), squareness (Br/Bs) and Magnetic Orientation Ratio (OR). Coercivity and squareness are parallel to the direction of travel of film through the magnets or of the magnet over the film.				40
45					45

TABLE 5

	<i>Series Number</i>	<i>Example or CE Number</i>	<i>Coercivity (Oersteds)</i>	<i>Squareness (Br/Bs)</i>	<i>Orientation Ratio</i>	
5	1	CE 1A Ex.26A	430 449	0.76 0.80	1.79 2.27	5
10	2	CE2A CE 3A Ex.27A	434 430 448	0.80 0.80 0.81	2.29 2.40 2.32	10
15	3	CE 4A CE 5A Ex.28A	657 671 690	0.68 0.78 0.80	1.46 2.07 2.10	15
20	4	CE 4A Ex.29A Ex.30A Ex.31A Ex.32A Ex.33A Ex.34A Ex.35A Ex.36A	699 712 727 723 723 713 716 716 718	0.69 0.79 0.81 0.78 0.81 0.79 0.82 0.81 0.78	1.30 1.79 1.83 1.85 1.77 1.73 1.86 1.80 1.82	20
25	5	CE 4A Ex.37A Ex.38A	708 739 745	0.68 0.77 0.81	1.31 1.80 1.89	25
30	6	CE 4A Ex.39A Ex.40A Ex.41A Ex.42A Ex.43A Ex.44A Ex.45A Ex.46A Ex.47A Ex.48A Ex.49A Ex.50A	707 736 738 733 749 739 742 744 744 737 727 728 722	0.68 0.77 0.79 0.78 0.82 0.77 0.80 0.80 0.82 0.80 0.79 0.78 0.79	1.39 1.78 1.85 1.74 2.00 1.79 1.90 1.88 1.87 1.79 1.70 1.83 1.71	30
35						35
40						40
45	7	CE 6A Ex.51A	425 431	0.76 0.82	2.02 2.44	45
	8	CE 7A Ex.52A	716 728	0.70 0.72	1.55 1.34	
50	9	CE 8A Ex.53A	465 474	0.61 0.61	1.22 1.22	50
55	10*	Ex.60A	154	0.48	1.43	55

* No comparative example in this series because of the failure to produce a dispersion using lecithin.

CLAIMS

- 60 1. A dispersion of finely divided particles of a magnetic material in an organic liquid containing a dispersant comprising an amine carrying a poly(carbonylalkyleneoxy) chain in which the alkylene groups contain up to 8 carbon atoms, or a salt thereof with an acid.
2. A dispersion according to Claim 1 wherein the magnetic material is selected from the magnetic oxides of transition metals and metal particles.

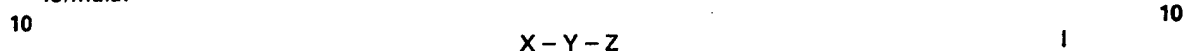
60

3. A dispersion according to Claim 2 wherein the magnetic oxides are selected from gamma-F₂O₃, Fe₃O₄, cobalt-doped iron oxides, CrO₂ and ferrites.

4. A dispersion according to any one of Claims 1 to 3 wherein the organic liquid is a solvent for a film-forming resin used as a binder for the magnetic particles or magnetic recording media.

5. A dispersion according to any one of Claims 1 to 4 wherein the organic liquid is selected from ketones, esters, ethers, and amides and mixtures thereof or mixtures with hydrocarbons and chlorinated hydrocarbons.

6. A dispersion according to any one of Claims 1 to 5 wherein the amine conforms to the general formula:



wherein

15 X is the poly(carbonylalkyleneoxy) chain;

Y is a bridging group; and

Z is an organic radical containing an amino group.

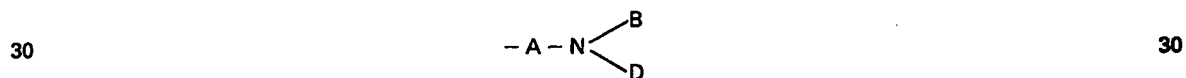
7. A dispersion according to any one of Claims 1 to 6 wherein the alkylene groups in the poly(carbonylalkyleneoxy) chain contain from 3 to 6 carbon atoms.

20 8. A dispersion according to Claim 7 wherein the alkylene groups are pentamethylene groups.

9. A dispersion according to any one of Claims 1 to 8 wherein the poly(carbonylalkyleneoxy) chain contains from 3 to 80 carbonylalkyleneoxy units.

10. A dispersion according to any one of Claims 6 to 9 wherein the bridging group, Y, is selected from -CO-O- (ester), -CO-NR (amide) and -CO-O⁻NT₃ (salt) in which R is H or C₁₋₂₀-alkyl and T is H or an organic radical.

11. A dispersion according to any one of Claims 6 to 10 wherein the organic radical containing an amino group, Z, is of the formula:



wherein

A is C₁₋₄-alkylene;

35 B is H or optionally substituted C₁₋₂₀-alkyl; and

D is optionally substituted C₁₋₂₀-alkyl.

12. A dispersion according to Claim 11 wherein B and/or D is selected from methyl, ethyl, lauryl, octadecyl, aminoethyl, aminoethylaminoethyl, hydroxyethyl, hydroxyethylaminoethyl, aminoethoxyethyl and poly(C₂₋₄-alkyleneimine).

40 13. A dispersion according to Claim 12 wherein B and/or D is polyethyleneimine having a molecular weight up to 600,000.

14. A dispersion according to any one of Claims 1 to 13 containing from 30% to 90% by weight of the magnetic material based upon the total weight of the dispersion and from 0.25% to 10% by weight on the dispersant based upon the weight of the magnetic material.

45 15. A dispersion according to any one of Claims 1 to 14 also containing up to 20% by weight of a film-forming resin based upon the total weight of the dispersion.

16. A process for the preparation of a dispersion according to any one of Claims 1 to 15 which comprises subjecting a mixture of the magnetic material, the dispersant and the organic liquid to a grinding operation to de-agglomerate the particles and reduce the particles of magnetic material to a length, along 50 their longest axis, not exceeding 5 microns.

17. A magnetic recording medium comprising a substrate carrying a superficial layer of a film-forming resin containing dispersed therein finely divided particles of a magnetic material and a dispersant as defined in any one of Claims 1 to 15.

18. A dispersant suitable for use in a dispersion according to Claim 1 comprising a poly(ethyleneimine) 55 carrying a poly(carbonylalkyleneoxy) chain attached thereto by an amide or salt bridging group, in which the alkyleneoxy groups contain from 3 to 6 carbon atoms and the poly(carbonylalkyleneoxy) chain contains from 3 to 80 carbonylalkyleneoxy groups.

19. A process for the preparation of a dispersant according to Claim 18 which comprises reacting poly(ethyleneimine) with a poly(carbonyl-C₃₋₆-alkyleneoxy) carboxylic acid, containing from 3 to 80 60 carbonyl-C₃₋₆-alkyleneoxy groups, at a temperature from 25°C to 250°C.

20. A process according to Claim 19 in which the poly(carbonyl-C₃₋₆-alkyleneoxy)carboxylic acid is prepared in situ by polymerisation of a hydroxyalkanecarboxylic acid or mixture thereof with an alkanecarboxylic acid in the presence of an esterification catalyst at a temperature from 100°C to 250°C.

21. A dispersant suitable for use in a dispersion according to Claim 1 comprising an acid salt of an amine carrying a poly(carbonylalkyleneoxy) chain attached thereto by an amide or salt bridging group, in which the alkyleneoxy groups contain from 3 to 6 carbon atoms and the poly(carbonylalkyleneoxy) chain contains from 3 to 80 carbonylalkyleneoxy groups.
- 5 22. A process for the preparation of a dispersant according to Claim 21 which comprises reacting the amine with an acid or an acidic salt or a quaternising agent at a temperature from 25°C to 250°C. 5

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